SOME ^{31}P NMR-DELICACY SERVED BY A FERROCENYL TETRAPHOSPHINE

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Polyphosphine ligands

Bulky, polydentate phosphines are commonly applied for transition metal-catalyzed (*e.g.* Heck or Suzuki) cross-couplings due to multifarious reasons[1]. Phosphines are 'soft' σ-donors, so able to solubilize and 'qualify' the metal centre for the first addition step with the oxidizing coupling reactant (*e.g*. an alkyl halide, see central figure). Besides, the bulkiness of the ligand facilitates the elimination of the product from the intermediate complex. Moreover, if several (phosphorus) coordinative sites are located permanently nearby the transition metal core, multiple coordination modes are possible what supplies high catalyst lifetime and efficiency.

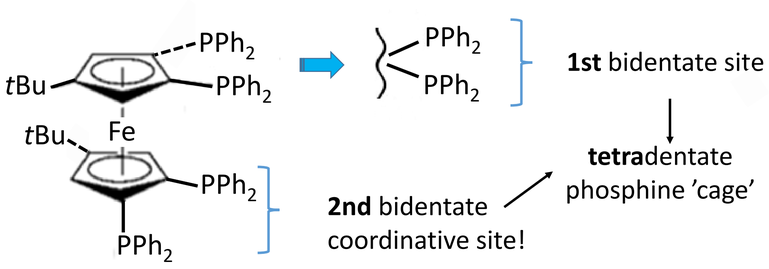
Objectives – The dynamics of polyphosphines

The longevity of such polydentate phosphine 'cage' requires local conformational rigidity. In other words, intramolecular rotations which would disrupt the advantageous arrangement have to be hindered (what is ensured by voluminous substituents, *e.g. t*Bu). However, if the system is investigated on a sufficiently long, *i.e.* 'NMR time scale', these decelerated motions might be observed. This work describes the investigation of a constrained ferrocenyl tetraphosphine ligand, Fc(P)$_4$*t*Bu which performed prominently in Pd-catalyzed Suzuki cross-coupling[1]. To demonstrate the structural background of the catalytic efficiency, our goal was to identify and quantitatively characterize the restricted conformational exchanges of the Fc(P)$_4$*t*Bu ligand and its stable [Pd(II)Br$_2$-Fc(P)$_4$*t*Bu] complex.

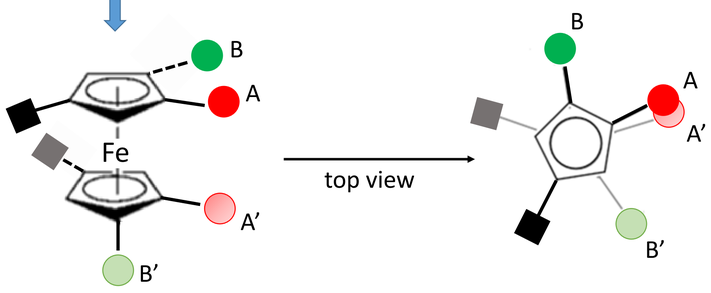
Methods

Once the samples were dissolved in toluene-d8, ^{31}P and ^{1}H NMR spectra were recorded at several temperatures between 213 K and 343 K. Dynamic phenomena were revealed by 1D ^{31}P and 2D ^{1}H EXSY experiments. The respective exchange rate constants (*k(T)*) could be assessed from the correlation with the mixing time (τ_m) and the intensity ratio of the exchange and irradiated peaks, *i.e.* $\frac{I_e}{I_i} = \frac{[1-\exp(-k\cdot\tau_m)]}{[1+\exp(-k\cdot\tau_m)]}$. In case of the Fc(P)$_4$*t*Bu the thermodynamic parameters ($\Delta S^{\#}, \Delta H^{\#}, \Delta G^{\#}$) for the discovered exchange process were also determined by linear least square fitting to the points of the Eyring plot[2] ($\ln(k\cdot T^{-1}/s^{-1}\cdot K^{-1})$ vs. T^{-1}/K^{-1} graph).

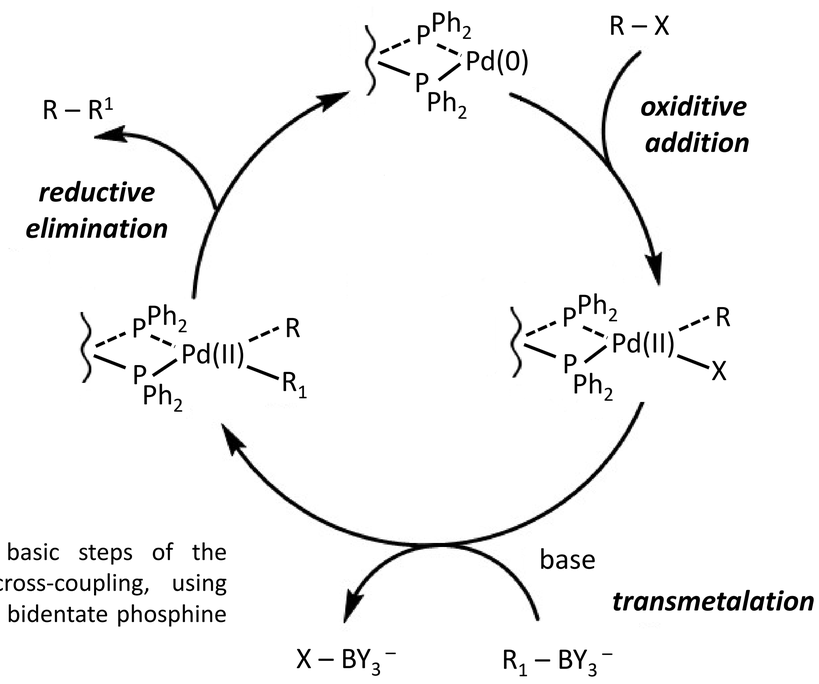
Results I – Fc(P)$_4$*t*Bu ligand



→ The Fc(P)$_4$*t*Bu ligand has two coordinative sites. The spatial vicinity of the two sites is fixed by the sterical repulsion between the *t*Bu groups. For better visibility, the substituents of the Fc-rings are symbolized with colored shapes and the ^{31}P chemical environments are marked with letters.

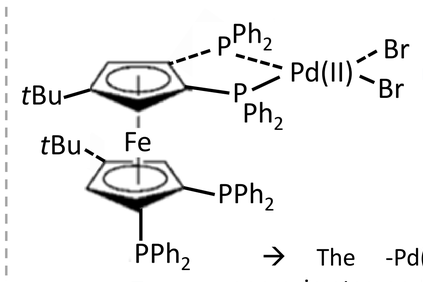


Suzuki cross-coupling



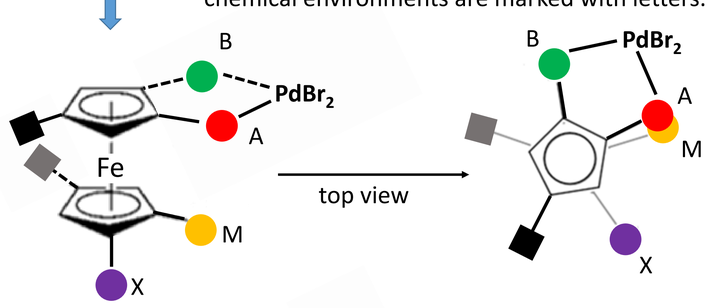
→ The basic steps of the Suzuki cross-coupling, using Pd and a bidentate phosphine ligand.

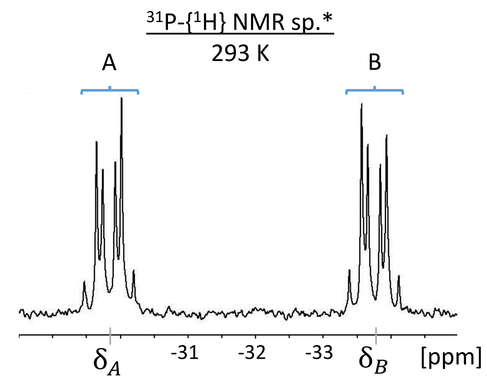
Results II – [Pd(II)Br$_2$-Fc(P)$_4$*t*Bu]



Fc(P)$_4$*t*Bu is a bidentate ligand for Pd.

→ The -Pd(II)Br$_2$ complex of Fc(P)$_4$*t*Bu approximates an intermediate state of the cross-coupling reaction cycle. For the [Pd(II)Br$_2$PPh$_2$] subunit, only the indicated square planar conformation is stable in the 16 e$^-$ state of Pd. For better visibility, the substituents of the Fc-rings are symbolized with colored shapes and the ^{31}P chemical environments are marked with letters.





So there are four ^{31}P-s in Fc(P)$_4$*t*Bu ...

→ ... but only two peaks in the ^{1}H-decoupled ^{31}P spectrum!

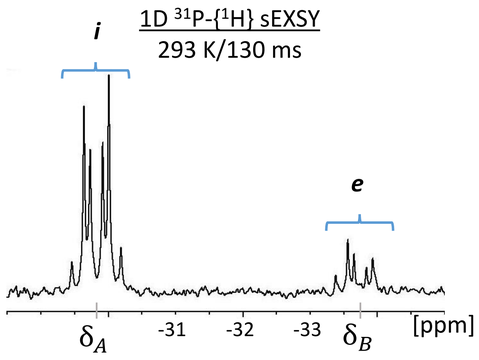
- The two centre (red circles) and two external (green circles) ^{31}P-s represent 1-1 chemical environment.

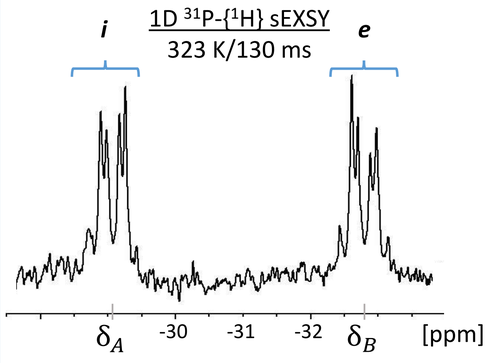
→ ... and in spite of ^{1}H-decoupling, we have puzzling multiplets!

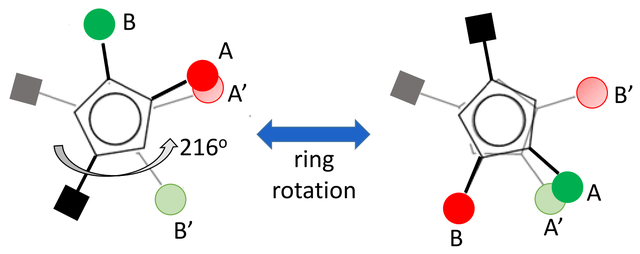
- Apparently, ^{31}P-^{31}P *through space* couplings are present (see the deduction of the coupling constant values in the Appendix) which result an **AA'BB' ^{31}P spin system!**

→ Additionally, 1D selective ^{31}P EXSY experiments (***i*** = irradiated peak, ***e*** = exchange peak) showed the exchange of the two chemical environments! (So the initially centred ^{31}P-s are periodically becoming the external ones and *vica versa*.)

- That is possible by the **relative rotation of the rings.**



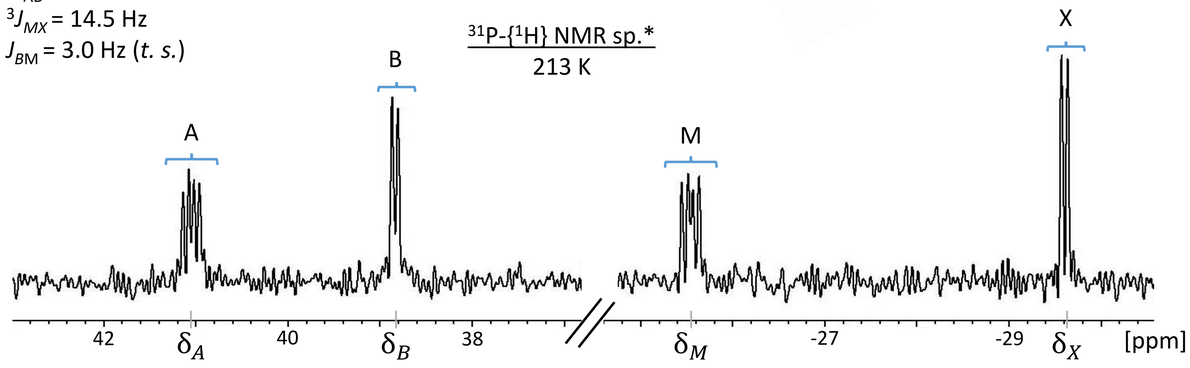




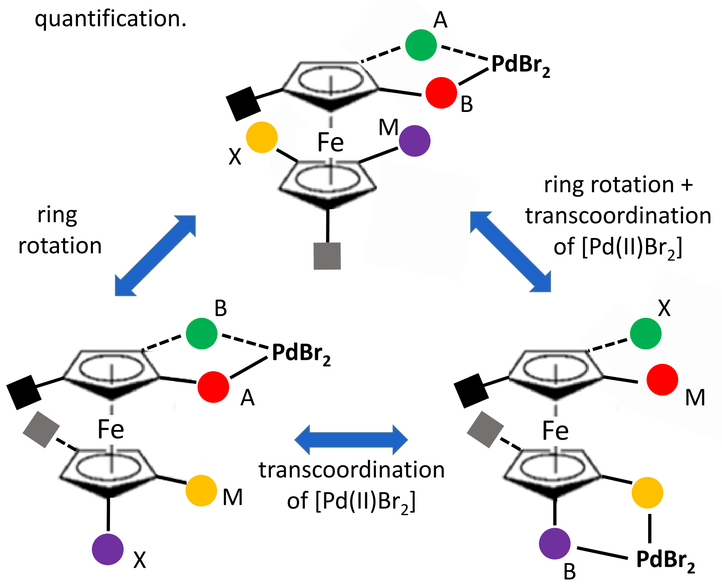
→ For example, k_{rot}(293 K)=3.30 s^{-1} and k_{rot}(323 K)=39.4 s^{-1}.

- From the intercept and the slope of the linear curve fitted to the points of the Eyring plot, $\Delta S^{\#}$= –23.6 J·mol^{-1}·K^{-1} and $\Delta H^{\#}$= 61.9 kJ·mol^{-1} could be calculated, respectively. Thus, the barrier height for the rotation of the rings is $\Delta G^{\#}$= 68.9 kJ·mol^{-1}.

J_{AM} = 25.2 Hz (*t. s.*)
$^{3}J_{AB}$ = 13.3 Hz
$^{3}J_{MX}$ = 14.5 Hz
J_{BM} = 3.0 Hz (*t. s.*)



→ There are distinct peaks for each phosphoruses in the ^{31}P spectrum, we have an **ABMX ^{31}P spin system**. Through space (*t. s.*) ^{31}P-^{31}P couplings are visible. ^{31}P-{^{1}H} sEXSY-s showed A ⟷ B and M ⟷ X exchanges at elevated temperature (above 323 K), so we have the **rotation of the rings** again! The S/N ratio was not sufficiently high for quantification.



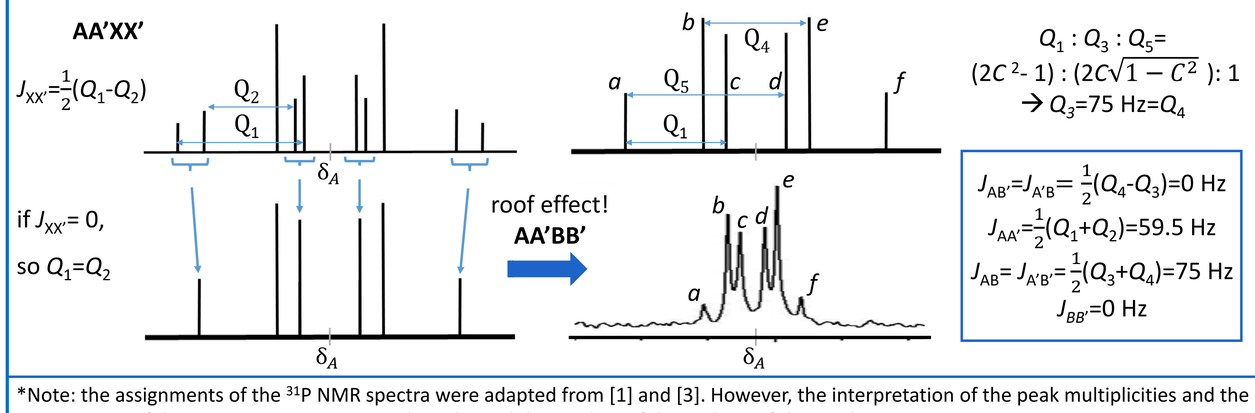
- For further inspection, a 2D ^{1}H-^{1}H EXSY was also recorded.

→ The exchange of protons belonging to the same Fc-ring showed a slower ring rotation compared to the likewise motion of the ligand itself (k_{rot}(323 K)=3.0 s^{-1}).

→ The exchange of protons belonging to different Fc-rings suggested the periodical **transcoordination** of the [Pb(II)Br$_2$] unit between the two Fc-rings. Again, the low intensity of the respective cross peaks impeded us from the calculation of k_{transc} (323K) and $k_{transc+rot}$ (323 K).

Appendix – How to derive the *J* values for our AA'BB' spin system?

For an AA'XX' system, 10 spin-allowed transitions compose a single multiplet at each chemical shift with individual frequencies, if $J_{AA'}$; $J_{XX'}$; J_{AX}=$J_{A'X}$; $J_{AX'}$=$J_{A'X'}$ are four non-equivalent and non-zero coupling constants (see top left corner).



$Q_1 : Q_3 : Q_5$= $(2C^2 - 1) : (2C\sqrt{1-C^2}) : 1$
→ Q_3=75 Hz=Q_4

$J_{AB'}$=$J_{A'B}$= ½(Q_4-Q_3)=0 Hz
$J_{AA'}$=½(Q_1+Q_2)=59.5 Hz
J_{AB}= $J_{A'B'}$=½(Q_3+Q_4)=75 Hz
$J_{BB'}$=0 Hz

*Note: the assignments of the ^{31}P NMR spectra were adapted from [1] and [3]. However, the interpretation of the peak multiplicities and the investigation of dynamic properties are novel results and the product of the authors of this work.

Conclusion and future prospects

In this work we identified and quantified a relative rotation between the two ferrocenyl rings of Fc(P)$_4$*t*Bu and of [Pd(II)Br$_2$-Fc(P)$_4$*t*Bu]. To confirm the direction of the rotation, the presented experimental data will be compared with the results of DFT calculations. In case of the complex, the periodic transcoordination of the [Pb(II)Br$_2$] unit illustrates the merit of multiple coordinate sites in polydentate phosphine ligands, *i.e.* their ability for the augmentation of catalytic efficiency. To assess exchange rates and thermodynamic parameters for the latter process, the signal to noise ratio of the NMR measurements has to be increased by *e.g.* applying 1D ^{1}H sEXSY-s or using more concentrated

References

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[3] Hierso, J-C., Fihri, A., Ivanov, V. V., Hanquet, B., Pirio, N., *et. al., J. Am. Chem. Soc.,* 2004, **126**, 11077-11087.

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